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X-ray reflectivity studies of the surface structure of liquid metals

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Abstract

Extensive theoretical predictions of atomic layering at the surfaces of liquid metals have remained unconfirmed due to the limited range of wave vector transfer q_z that has been previously measured. We report here on X-ray reflectivity studies from the surfaces of liquid mercury to $q_z \gtrsim 2.8$ Å^{-1}, and gallium to $q_z \gtrsim 3.0$ Å^{-1}, that show peaks which clearly demonstrate atomic layering with spacing on the order of the atomic diameter. The exponential decay of layer penetration into the bulk for Ga (6.5 Å) is larger than for Hg (3–3.5 Å). The prominent features of the layering remain unchanged under self-assembled monolayers of thiols. The Ga layering shows an unexpected strong temperature dependence. Differences between the reflectivity from Ga and Hg at small q_z indicate fundamental differences in the surface structure for these two liquid metals.

The primary difference between liquid metals and simple dielectric liquids like water, oils and alcohols is that the metals consist of two charged interacting liquids: a classical ion liquid and a quantum free-electron liquid [1,2]. The dominating Coulombic interactions of the liquid metal are orders of magnitude larger than the van der Waals interactions that prevail in the simple dielectric liquids. A well-known manifestation of these differences is the 10–50-fold larger surface tension of liquid metals [3,4]. An important further consequence of these differences is the theoretical prediction that for liquid metals, atoms near the surface will be ordered in layers parallel to the surface [3,5–8]. The effect is predicted to decay exponentially with increasing distance from the surface, with a characteristic length of a few atomic diameters. Although this prediction is now over two decades old it was hitherto not tested experimentally, in spite of substantial efforts by several groups worldwide [9–11].

In a series of experiments we recently succeeded in unambiguously measuring this effect in liquid mercury [12] and gallium [13] with atomic scale resolution. Significant differences were found in the decay length and ordering properties of these two liquids. Furthermore, in the most recent experiments the layering in gallium was found to exhibit an unexpected temperature dependence. In mercury, we found that self-assembled thiol monolayers at the surface do not influence the layering. These results provide strong confirmation for the prevailing theoretical understanding of the effective interactions in liquid metals but also raise important

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additional questions resulting from several unexpected observations.

X-ray reflectivity measurements were made at NSLS on the bending magnet beam line X22B using the Harvard/BNL liquid surface reflectometer ($\lambda \approx 1.2$ Å) [14], and on the insertion device beam line X25 using a new reflectometer ($\lambda \approx 0.65$ Å) that is described elsewhere [15, 16]. In these measurements the primary signature of surface layering is the appearance of a broadened peak in the reflectivity at a wave vector, $q_z = 2\pi/a$ where a is of order of the molecular spacing. For liquid metals, where $a \approx 3$ Å, this necessitates measurements out to $q_z > 2$ Å^{-1}. The reflectivity at these large q_z is weak and mandates the use of a synchrotron source. Previous measurements on Hg [10] did not extend past $q_z = 0.75$ Å^{-1}, and thus could not show unambiguous proof for layering.

Fig. 1 shows the absolute reflectivity $R(q_z)$ of liquid mercury obtained under a hydrogen reducing environment at room temperature [12]. The solid line is the theoretical reflectivity $R_F(q_z)$ for a perfectly flat surface, calculated from the Fresnel law of optics. The reflectivity falls from close to unity below the critical angle to 10^{-9} at $q_z \approx 2.8$ Å^{-1}, yet it remains within a factor of two of $R_F(q_z)$ for $q_z < 2.3$ Å^{-1}. This clearly indicates a surface roughness smaller than the atomic diameter. The position of the broad peak at $q_z = 2.15$ Å^{-1} is close to that of the bulk liquid structure factor and resembles similar features found in reflectivity measurements of surface-induced layering in liquid crystals [17]. This clearly indicates an atomic layering at the surface of mercury.

For a structured interface, the ratio between the measured reflectivity, $R(q_z)$, and the Fresnel reflectivity, $R_F(q_z)$, deviates from unity, and in the weak scattering approximation simplifies to

$$R(q_z) \approx R_F(q_z) \left| \rho_\infty^{-1} \int \mathrm{d}z \, \frac{\partial \langle \rho(z) \rangle}{\partial z} \, \mathrm{e}^{\mathrm{i}q_z z} \right|^2,$$

where $\langle \rho(z) \rangle$ is the average electron density along the surface normal and ρ_∞ is the bulk density [17]. A physically appealing model of the liquid vapor interface, $\langle \rho(z) \rangle$, is obtained from a truncated solid model in which the root-mean-square (rms) deviations of atoms in each layer increases with increasing distance from the interface [12]. Layering occurs when the rms displacements at the surface are less than the inter atomic spacing. When the rms displacements increase as the square root of the distance, the model gives an exponential decay of the layering amplitude. By fitting the reflectivity to this model, the Hg surface density profile, shown as the inset in Fig. 1, is obtained. It clearly demonstrates surface-induced layering with an exponential decay length of 3.5 Å.

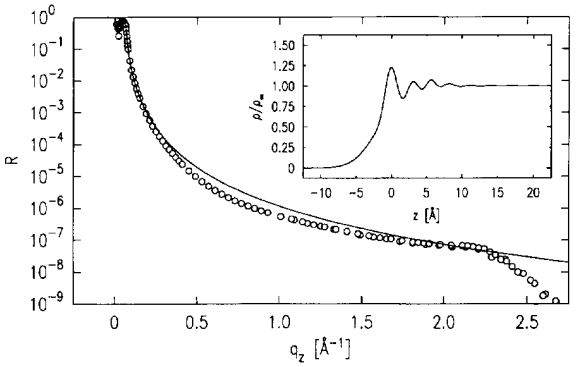

Fig. 1. X-ray reflectivity from the Hg/vapor interface at room temperature (circles), and the Fresnel reflectivity (solid line). The surface normal density profile, obtained from the reflectivity analysis, is shown in the inset.

The topmost layer rms deviations (less than 1 Å) agree very well with those calculated using the thermally excited capillary wave model of surface roughness [18, 19]. In addition, this density profile gives a topmost layer spacing which is expanded with respect to the underlying layers by several tenths of an Ångstrom. Similar lattice expansions have been observed at reconstructed solid metal surfaces [20–22]. The Hg topmost layer expansion, along with a slightly asymmetric topmost layer density, is one model that does give rise to the maximum deviations from the Fresnel law at about 0.6 Å^{-1}.

One simple physical picture of surface-induced layering consists of a local "surface field" that induces layering near the surface, coupled to the susceptibility of the bulk liquid. For example, as the temperature of a nematic liquid crystal approaches the transition temperature to the bulk smectic A phase, a growth of surface layers is induced at the surface. The penetration length of this layering into the bulk nematic phase is identical to the bulk correlation length $\xi_\parallel(T)$ [23]. In order to examine the possibility of a similar surface behavior for the liquid metal surface, in Fig. 2, we show the bulk correlation function along with the density profile that is obtained from Fig. 1 after deconvoluting the contribution of the thermal capillary waves to the interfacial width. Beyond about 4 Å there is excellent agreement between the bulk pair correlation function and the surface profile. This supports the notion that the short-range order in bulk mercury and the layering at its surface are closely related and, in turn, indicates that the latter is primarily a simple geometric consequence of the physical requirement to form a sharp interface. Deviations at small distances are in part due to the restricted interpenetration occurring around individual atoms which increases the amplitude of the first peak in bulk pair correlation function.

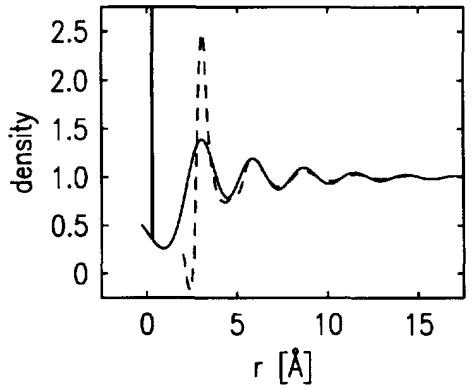

Fig. 2. The Hg bulk pair correlation function and the surface normal density profiles. Note that the two are nearly indistinguishable for distances greater than 4 Å.

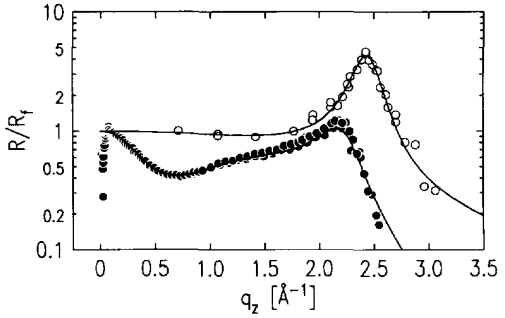

Fig. 3. The normalized reflectivity R/R_F for Hg (filled circles) and for Ga (open circles) at room temperature. The Ga measurements were carried out at beam line X25 at the NSLS.

Gallium has several unique qualities that distinguish it from Hg and most other liquid metals. When compared to Hg, Ga has a smaller atomic diameter, much higher surface tension, an extremely small vapor pressure, an exceptionally large liquid range (approx. 2000°C), a large supercooling range (approx. 30°C), and short distance bond orientational correlations. It is not clear to what extent variations in bulk properties manifest themselves at the free surface. In Fig. 3 we show the normalized reflectivity from the sputtered clean liquid Ga surface in UHV at ~22°C [13], which is supercooled by 8°C, along with the corresponding normalized Hg reflectivity obtained from Fig. 1. Below 2.0 $Å^{-1}$ the Ga reflectivity shows no appreciable deviation from the Fresnel theory, in contrast to the dip observed for Hg. The quasi-Bragg peak, which is at 2.4 $Å^{-1}$ for Ga and is narrower than in Hg, indicates that the surface layering decay length is significantly larger in Ga. Fits to the density profile described above, confirm this expectation and give an exponential decay length of 6.5 $Å^{-1}$. This length is a factor of two larger than both the Hg surface layering length and the Ga bulk pair correlation function decay length.

It is important to note that although the liquid phase of Hg is stable at room temperature (22°C), Ga is only liquid at this temperature as a metastable supercooled phase. Although there is no theoretical prediction that the surface order of the supercooled phase should be different from that of the stable phase, we have recently carried out measurements of the Ga surface between 22 and 180°C [24]. Much to our surprise the height of the peak at $q_z \approx 2.4$ $Å^{-1}$, which is $R(q_z)/R_F(q_z) \approx 4$ at room temperature, decrease to ≈ 1.2 at 180°C with no accompanying variation in the width of the peak. This indicates that the layering decay length is independent for these changes in temperature, but the amplitude of the density variation is reduced with increasing temperature. The physical origin of this unexpected behavior is currently under study.

To assess the influence of overlayers on the layering effect, we have studied self-assembled monolayer films of thiol molecules (a sulfur terminated alkane chain) on the liquid Hg surface [25]. Clear modulations were observed in the reflectivity curve, indicating a densely packed monolayer whose thickness is commensurate with the fully extended, vertically oriented thiol molecule. Remarkably, essential features of the reflectivity, including the quasi-Bragg peak and the dip at small q_z are identical with and without the thiol monolayer. This clearly indicates that the surface layering is an intrinsic feature of the Hg surface. Further measurements are in progress to elucidate the detailed structure of the thiol monolayer, and its molecular length and temperature dependence.

Acknowledgements

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